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㉖ **Pressure-sensitive conductive elastomer compound.**

㉗ Baked and carbonized conductive spherical particles of a macromolecular material are incorporated and dispersed into a matrix material having insulating and elastomeric properties. The conductivity of the conductive particles varies according to the degree of their carbonization. The resulting compound exhibits high resistance (insulating performance) when it is in non-pressed condition and, as the compound is pressed, its resistance varies according to the magnitude of the pressure.

EP 0 223 355 A1

PRESSURE-SENSITIVE CONDUCTIVE ELASTOMER COMPOUND

This invention relates to pressure-sensitive conductive elastomer compounds and, more specifically, to a pressure-sensitive conductive elastomer compound of the type which exhibits high resistance (insulating performance) when it is in non-pressed condition, and of which the resistance, as the compound is pressed, will vary according to the magnitude of the pressure.

Hitherto, pressure-sensitive conductive materials have been known which are in the form of a compound comprising a resilient material, such as rubber or the like, and a conductive filler mixed therewith. In this

respect, metallic particles, such as nickel, conductive carbon black, graphite particles and the like are normally used as the filler. Such conductive compounds, moulded into rod or sheet form, are widely used today
5 as switching elements, or as pressure-sensitive elements for sensors such as pressure sensors and tactile sensors.

A number of problems are associated with conductive compounds of the aforesaid conventional type. Those incorporating metallic particles as a conductive filler
10 are liable to a change of properties with time due to oxidation of the particles. Thus, such compounds lack stability and are often subject to chattering and noise generation. Those incorporating powdery masses of conductive carbon black as a conductive filler exhibit
15 insignificant change in resistance when they are under pressure, because the particle diameter of the carbon black is extremely small, i.e. only 20 to 30 μ . As such, these latter compounds are of no practical use. Finally, if a granulated material formed of conductive carbon
20 black is used as a filler, it is possible to obtain greater variations in resistance, but a conductive compound incorporating such material is liable to particle breakage when it is under pressure. Thus, such compound lacks both durability and stability.

If graphite particles are used as a conductive filler, no characteristic stability can be obtained if they are of non-uniform shape, as in natural graphite. Therefore, it is known to use artificial graphite particles which have been rounded and freed of sharpness by pulverization, or milling, or otherwise, to provide good characteristic stability. Conductive compounds incorporating artificial graphite particles of such type are advantageous in that they are characteristically stable, durable, and less liable to noise generation than other types of compound. On the other hand they have drawbacks in that preparation of graphite particles to the desired configuration requires a complicated and troublesome procedure and in that the attainable yield thereof is rather low.

In view of the aforesaid difficulties with the prior-art compounds, this invention has as its primary object the provision of a pressure-sensitive conductive elastomer compound which has high stable conductive characteristics under pressure and which is also easy to manufacture.

Another object of the invention is to provide a pressure-sensitive conductive elastomer compound whose conductive characteristics under pressure may be varied without changing the mechanical properties of the compound.

In order to accomplish the above and other objects, the compound according to the invention comprises a matrix material having insulating and elastomeric

properties, and conductive particles incorporated and dispersed into the matrix material, characterised in that the conductive particles consist of baked and carbonized spherical particles of a macromolecular material.

Materials which may be used as the aforesaid matrix material having insulating and elastomeric properties include natural rubber; synthetic rubbers, such as chloroprene rubber, SBR, NBR, and silicone rubber; thermoplastic elastomers, such as polyurethane, polyester, and EVA; and liquid rubbers, such as polyurethane and silicone. Particularly preferable among them is silicone rubber, a material having high heat resistance, excellent electrical properties, and good resistance to chemicals.

Macromolecular materials having a spherical particle configuration useful for the purpose of the invention include styrene, vinylchloride, vinylidenechloride, methyl methacrylate, and furfuryl alcohol, all prepared in spherical particle form by suspension polymerization, and resol resins chemically pulverized into spherical particle form.

The term "suspension polymerization" referred to

herein means a process wherein a polymerization catalyst is added to monomers, the mixture being stirred in water with a dispersant added to allow the monomers to disperse in oil-drop form and then being polymerized.

- 5 The term "chemically pulverized" referred to herein means a process whereby a resin dissolved in a solvent is cooled or added to a precipitant so that the resin is separated out in fine powder form.

10 The particle diameter of the conductive particles in the compound of the invention is advantageously from 30 to 120 μm , preferably from 50 to 100 μm , and the proportion of the particles to the compound as a whole is preferably 20% to 60% by volume. If the particle diameter is less than 30 μm , the possible variation in
15 resistance of the compound is extremely small, while if it is greater than 120 μm , the particles cannot satisfactorily be dispersed in the matrix material. The proportion by volume of the particles may be suitably determined according to the desired characteristics and sensitivity
20 of the compound, and also taking into account the type of matrix material. However, if it is less than 20% by volume, the compound may not exhibit sufficient conductivity, and if it is more than 60% by volume, the variation in conductivity (resistance) when the compound is under
25 pressure, from the conductivity level when the compound is not under pressure, is insignificant, the compound being thus of no practical use. Therefore, the proportion of the particles should be within the range of 20 vol % to 60 vol %.

In accordance with the invention, the spherical particles of a macromolecular material have conductivity imparted to them by being baked and thereby wholly or partially carbonized. This process facilitates
5 the selection of particles size for the conductive particles. It is thus possible to use particles having a uniform particle size, and thereby obtain a compound having highly stable pressure-sensitive conductive properties. Furthermore, the compound is easy to
10 manufacture.

The degree of carbonization of the particles (i.e. the thickness of the carbonized portion of each particle's spherical shell) can be varied by changing the degree of baking of the particles, and thus particles of varying
15 grades of conductivity can be easily produced. It is, therefore, possible to obtain differing pressure-sensitive conductive characteristics without changing the mechanical properties of the compound.

The invention will be described further, by way of
20 example, with reference to the accompanying drawing, in which:

Figs. 1a to 1c, inclusive, are sectional illustrations showing various degrees of carbonization of

spherical particles of a macromolecular material as incorporated in exemplified compounds in accordance with the invention. In Fig. 1a, only the surface area of the particle is carbonized. In Fig. 1b, almost
5 the entire particle is carbonized. In Fig. 1c, the particle is entirely carbonized;

Fig. 2 is a graph showing the pressing force-resistance relationships in Example 1; and

Fig. 3 is a graph showing the pressing force-
10 resistance relationships in Examples 2 and 3, in which graph the reference character (a) represents such relationships in Example 2 and the reference character (b) represents those in Example 3.

Figs. 1a, 1b and 1c are schematic views showing a
15 few examples of spherical carbonized particles used for the purpose of the invention. Particles of various grades of conductivity are shown as they are formed from non-conductive spherical particles of a macromolecular material. Experiments have revealed that the electric
20 conductivity of the particles varies according to the heating and baking conditions. This is considered to be attributable to the following facts. If, as in Fig. 1a, only a region around the outer periphery of a particle 1

is carbonized to a thickness (t) in a spherical shell pattern, the conductivity of the particle 1 is low because the carbonized portion 2, i.e. the portion having electric conductivity, is of a small volume
5 relative to the total volume (the non-carbonized portion being designated by reference numeral 3). If carbonization progresses further to the extent that a larger part of the particle 1 is carbonized, as shown in Fig. 1b, the conductivity of the particle 1 becomes
10 considerably greater. Finally, if carbonization progresses still further until the particle is completely carbonized, the conductivity of the particle is maximised. Thus, even if particles 1 of the same diameter are used, the degree of carbonization of the particles varies
15 according to the baking conditions applied. These facts are considered to be responsible for the variations in conductivity which can be obtained in different embodiments of the invention.

The degree of carbonization of the particles 1 is
20 adjustable by changes in baking conditions, such as heating temperature and time. Therefore, by baking and carbonizing preselected particles 1 of a specified diameter under preset baking conditions it is possible

to obtain quite easily, particles 1 having the required conductivity.

Particular examples are given hereinbelow to further illustrate the invention.

5 EXAMPLE 1

Spherical particles of a polystyrene resin material cross-linked with divinylbenzene and having a particle diameter of about 70 to 130 μm were heated to 300°C in an air current, then heated and baked to 1000°C in an inert
10 gas. The particle diameter measurements of the carbonized particles thus obtained showed that more than 90 2wt% of the particles prior to baking were within the range of 53 to 105 μm . One hundred parts by weight of the carbonized particles within this diameter range were
15 mixed with 100 parts by weight of a silicone rubber (TSE 270 - 4 U, produced by Toshiba Silicone Co.), the mixture being kneaded, and one form of the pressure-sensitive conductive elastomer compound according to the invention was thus produced.

20 The compound was moulded by press-moulding into a sheet having a thickness of 0.5 mm. Pressure was applied to the sheet surface by a rod-like pressing

electrode having a 5 mm diameter, and the relationships between the pressing force and the resistance were measured. The measurements, as shown in Fig. 2, revealed satisfactory resistance variation characteristics, 5 with only a small degree of hysteresis.

In this example, the fine spherical particles of polystyrene resin were produced in the following way. Benzoyl peroxide or lauroyl peroxide was dissolved in a mixed monomer liquid of styrene and divinylbenzene, and 10 the resulting liquid was vigorously agitated in water to which a dispersant, such as completely-saponified polyvinylalcohol, non-completely-saponified polyvinyl-alcohol or the like had been added, then suspension-polymerized at 80°C for 6 to 8 hours.

15 EXAMPLE 2

A phenolic resin having a spheric particle configuration and a particle diameter of about 60 to 100 μm was heated and baked at 800°C in an inert gas. The particle diameters of the carbonized spherical particles 20 thus obtained in glass-like (amorphous) form were such that more than 90 wt % of the particles prior to baking were within the range of 44 to 74 μm . One hundred parts by weight of the carbonized particles within this range

were mixed with 100 parts by weight of same silicone rubber as in Example 1, the mixture being kneaded together, then moulded by press moulding into a sheet having a thickness of 0.5 mm.

5 Pressing force-resistance characteristics were measured in same way as in Example 1. The measurements, as shown in Fig. 3 graph (a), revealed that the sheet had good characteristics, with a small degree of hysteresis.

10 In this example, the spherical phenolic resin particles were produced in the following way. A resol resin was dissolved in acetone, and a precipitant was added to the mixture during stirring, so that fine spherical resin particles were separated out. The
15 particles were then subjected to filtration and drying and subsequently heated and hardened.

Spherical phenolic resin particles were also produced in the following way. Phenol was added to a large amount of an aqueous solution of hydrochloric
20 acid and formaldehyde during stirring, whereby solid matter having a spherical configuration was produced. The solid matter was separated out, then neutralized in an alkaline solution, and subsequently washed in

water and dried. Use of the phenolic resin particles thus obtained also gave satisfactory results as in aforesaid case.

EXAMPLE 3

- 5 Spherical phenolic resin particles identical with those used in Example 2 were heated and baked at 600°C. The particle diameters of the glass-like spherical carbonized particles were such that more than 90 wt % of the particles prior to baking were within the diameter
- 10 range of 44 to 74 μm . One hundred and twenty parts by weight of the carbonized particles within this range were mixed with 100 parts by weight of same silicone rubber as in Example 1, the mixture being kneaded together and a 0.5 mm thick sheet was produced by press-moulding.
- 15 Measurements were made in same way as in Example 1. The results are shown in Fig. 3 graph (b). In this instance, the variations in resistance shown are of a similar pattern to those in Example 2 except that the range of variations is different. This indicates that
- 20 the conductivity of the spherical phenolic resin particles varies according to the baking temperature for the particles. Presumably, this is due to the fact that the degree of carbonization varies according to the baking

temperature and that as the baking temperature becomes higher, the carbonized portion of each particle will become greater. In other words, it is considered that the thickness (t) of the carbonized spherical shell portion in Fig. 1a becomes greater at a higher baking temperature and as the carbonized portion is increased so the conductivity of the particle is increased.

CLAIMS

1. A pressure-sensitive conductive elastomer compound comprising a matrix material having insulating and elastomeric properties, and conductive particles (1) incorporated and dispersed into the matrix material, 5 characterised in that the conductive particles (1) consist of baked and carbonized spherical particles of a macro-molecular material.
2. A compound according to claim 1 wherein the particle diameter of the conductive particles (1) is from 30 to 10 120 μm .
3. A compound according to claim 1 or 2 wherein the proportion of the conductive particles (1) relative to the entire compound is from 20% to 60% by volume.
4. A compound according to claim 1, 2 or 3 wherein the 15 matrix material is silicone rubber.
5. A compound according to any preceding claim wherein the conductive particles (1) consist of baked and carbonized spherical particles of a polystyrene resin or a phenolic resin.

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Fig.1a

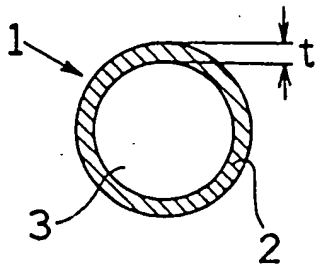


Fig.1b

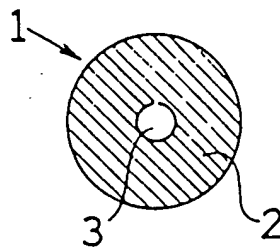


Fig.1c

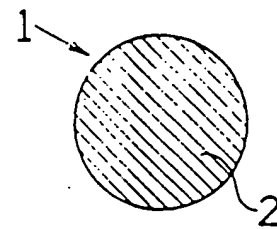


Fig.2

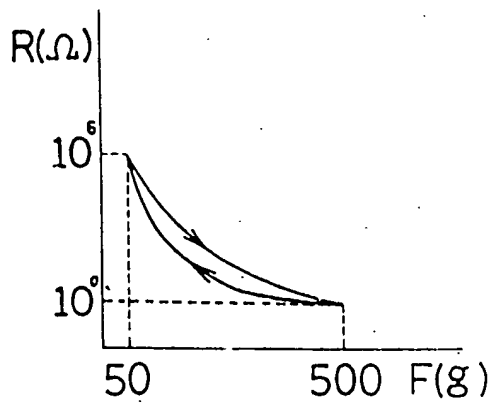
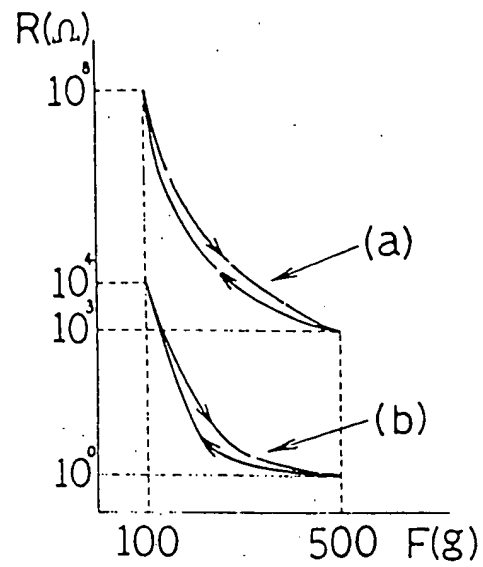


Fig.3





European Patent
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EUROPEAN SEARCH REPORT

0223355
Application number

EP 86 30 7049

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	FR-A-2 537 984 (DENKI KAGAKU KOGYO) * Claims 1-5; page 5, lines 32-36; page 6, lines 1-4; page 8, lines 12-15 *	1,3-5	H 01 B 1/24
X	FR-A-2 450 856 (TORAY SILICONE) * Claims 1-7; page 6, lines 1-8 *	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			H 01 B 1/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-01-1987	Examiner DROUOT M.C.
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